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54) Binder mixture consisting of sulfate, calcium-donating and pozzuolanic substances

A binder mixture consisting of sulfate, calcium-donating and pozzuolanic substances leads to hardening products, which have relatively high initial strength, depending on the mixing ratio, no post-softening that is typical for gypsum and have higher final strength through hydraulic post-hardening. In order to provide a dimensionally stable hardening process, the ratio of calcium-donating to pozzuolanic components must not exceed 0.75.

(33 30 406)

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Patent Claims:

1. Binder mixture of sulfate, calcium-donating and low-calcium pozzuolanic substances, characterized by the fact
that it consists of 50 to 90 weight percent of calcium sulfate, 3 to 25 weight percent of calcium-donating substances and 5 to 35 weight percent of pozzuolanic substances.

2. Binder mixture according to Claim 1,
characterized by the fact
that it contains an aluminosilicate-type pozzuolana.

3. Binder mixture according to Claim 1,
characterized by the fact
that it contains hemihydrate gypsum plaster as sulfate component.

4. Binder mixture according to Claims 1 and 3,
characterized by the fact
that it contains Portland cement as hydraulic component.

5. Binder mixture according to Claims 1, 3 and 4,
characterized by the fact
that it contains trass meal as pozzuolanic component.

6. Binder mixture according to Claims 4 and 5,
characterized by the fact
that the weight ratio of trass meal to Portland cement is within the limits of 1 to 2.

7. Binder mixture according to Claims 1 to 6,
characterized by the fact
that the processing and application properties are modified by additives.

8. Application of the binder mixture according to Claims 1 to 7,
characterized by the fact
that the first phase of the hardening, which proceeds in two phases in time, occurs with the application of pressure.

9. Application of the binder mixture according to Claims 1 to 8,
characterized by the fact
that a part of the still free water is bound chemically by the reaction products formed in the second hardening phase.

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Binder mixture consisting of sulfate, calcium-donating and pozzuolanic substances

The invention is concerned with a binder mixture consisting of sulfate, calcium-donating and pozzuolanic substances.

It is known that sulfate binders, for example, baked gypsum, may be mixed only with very small amounts (< 4%) of hydraulic additives, for example, Portland cement, since they are not compatible. If larger amounts are added, then binder mixtures are obtained which harden not retaining their dimensions, and therefore are unsuitable for application. The reasons for this are the water-rich calcium aluminate sulfate hydrates, which are formed under conditions of high calcium concentration, which leads to significant expansion phenomena after hardening. Furthermore, it is known (DE-AS 1 241 330) that binder mixtures consisting of calcium sulfate, cement and silicate additives of sedimentary origin, for example, tripoli powder and diatomaceous earth do not exhibit these disadvantages. When making up the binders with water, first the calcium sulfate half hydrate becomes hydrated to the dihydrate, while in a significantly later phase, the reactions between the calcium of the "cement" of the silicic acid of the acid silicate additives, and the water form waterproof [water-resistant?] calcium silicate hydrates. The reactions between gypsum, cement and pozzuolanas, which lead to the so-called calcium aluminate sulfate hydrates, are to be avoided in this way because they are generally known to be destructive. However, it is overlooked here that such compounds, when their formation is limited to the initial phase of the hardening, to the so-called liquid phase, are not destructive, but they promote strength. The following results, which were obtained on standard test specimens of a binder mixture according to the invention, according to Practical Example 1, illustrate this for bending and compressive strength evolution of standard prisms under comparable conditions with inhibited drying:

storage and hardening time	bending strength (N/mm²)		compressive strength (N/mm²)	
	gypsum	gypsum-cement-pozzuolana	gypsum	gypsum-cement-pozzuolana
2 h	2.04	2.06	3.91	4.25
1 d	2.02	1.91	2.84	4.15
3 d	1.83	1.92	3.50	3.94
7 d	1.80	2.07	2.95	3.92
14 d	1.74	1.98	2.90	5.07
28 d	1.80	2.45	3.11	6.23

Thus, according to the invention, the conditions required for increasing the strength are created by the choice of a suitable ratio of the calcium-donating and calcium-binding components, which, in the initial phase of hardening, ensure the high calcium concentration necessary for the formation of calcium aluminate sulfate hydrates, but, during the further progress of the hardening, decrease the calcium concentration to the extent that the formation of destructive calcium aluminate sulfate hydrates is avoided.

The task of the invention is to develop binder mixtures, the processing properties of which, especially the early strength, are determined predominantly by the sulfate component, through the formation of calcium sulfate dihydrate and calcium aluminate sulfate hydrate, the application properties of which, especially the final strength and the resistance to water, are significantly determined by the reaction products of the calcium-donating hydraulic and calcium-forming pozzuolanic components. With the aid of these binder mixtures, it is made possible to produce structural parts which reach rapidly a strength where they can be handled and have improved final and wet strength in comparison to pure gypsum products.

According to the invention, this task was solved, according to the characterizing part of Claim 1. Further advantageous embodiments of the invention are described in the Subclaims 2 to 9.

The hardening of such binder mixtures, when making up with water, proceeds in two different phases as a function of time. In the initial phase, it is based on the hydration of the

calcium sulfate to calcium sulfate dihydrate and calcium aluminate sulfate hydrate, and during the hydraulic post-hardening it is based on reactions between the calcium of the hydraulic component and the aluminates or silicates of the pozzuolanic component. Since the hydraulic post-hardening extends over a longer period of time, a part of the free water still present is bound as hydrate water, so that, in the case of water-binder ratios $w \leq 0.45$, for example, in a half-dry method using water depots (see DE-AS 29 19 311), technical drying of the end-product can be omitted.

The progress of hardening during the first phase and the elasto-mechanical properties of the hardened products can be changed by adding suitable additives to the binder mixture.

The invention is explained below in more detail with the aid of 4 practical examples.

Example 1:

Binder, produced by grinding together and/or mixing, consisting of:

70 parts by weight of hemihydrate gypsum plaster and/or gypsum plaster according to DIN 1168

15 parts by weight of trass cement according to DIN 1164

15 parts by weight of trass meal according to DIN 51 043

Example 2:

Binder, consisting of:

70 parts by weight of hemihydrate gypsum plaster and/or gypsum plaster according to DIN 1168

12 parts by weight of Portland cement or Portland clinker according to DIN 1164

18 parts by weight of trass meal according to DIN 51 043

Example 3:

Binder, consisting of:

60 parts by weight of hemihydrate gypsum plaster and/or gypsum plaster according to DIN 1168

13 parts by weight of Portland cement according to DIN 1164

27 parts by weight of trass meal according to DIN 51 043

Example 4:

Binder, consisting of:

60 parts by weight of enstrich plaster and/or gypsum plaster according to DIN 1168

25 parts by weight of trass cement according to DIN 1164

15 parts by weight of trass meal according to DIN 51 043

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54) **Binder mixture consisting of sulfate, calcium-donating and aluminate-rich pozzuolanic substances**

57) A binder mixture consisting of sulfate, calcium-donating and pozzuolanic substances leads to hardening products which have relatively high initial strength, depending on the mixing ratio, no post-softening that is typical for gypsum, and have higher final strength through hydraulic post-hardening. In order to provide a dimensionally stable hardening process, the ratio of calcium-donating components to pozzuolanic components must not exceed 0.75.

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Binder mixture consisting of sulfate, calcium-donating and aluminate-rich pozzuolanic substances

The invention is concerned with a binder mixture consisting of sulfate, calcium-donating and aluminate-rich pozzuolanic substances.

It is known that sulfate binders, for example, baked gypsum, may be mixed only with very small amounts (< 4%) of hydraulic additives, for example, Portland cement, since they are not compatible. If larger amounts are added, then binder mixtures which harden without retaining their dimensions are obtained, and therefore are unsuitable for application. The reasons for this are the water-rich calcium aluminate sulfate hydrates, which are formed under conditions of high calcium concentration, which can lead to significant expansion phenomena during and after hardening. Furthermore, it is known that binder mixtures consisting of calcium sulfate, cement and silicic-acid-rich pozzuolanes of natural origin (DE-AS 1 241 330), for example, tripoli powder and diatomaceous earth, as well as of synthetic origin (DD-PS 140-245), do not exhibit these disadvantages. When making up such binders with water, first the calcium sulfate hemihydrate becomes hydrated to the dihydrate, while in a significantly later phase, reactions between the calcium of the cement, of the silicic acid of the acid silicate additives and the water, result in the formation of waterproof [water-resistant?] calcium silicate hydrates. The reactions between gypsum, cement and pozzuolanas, which lead to the so-called calcium aluminate trisulfate hydrates, are undesirable because of their destructive effects and are avoided to greatest possible extent by the use of substances of low alumina content.

Due to the feared formation of ettringite, pozzuolanes with higher alumina content are unsuitable for the production of gypsum-cement-pozzuolane binders and cannot be used for practical purposes.

The goal of the invention is to overcome the deficiencies of silicate-rich pozzuolanas and the high-energy consumption in their synthetic manufacture and to make it possible to produce binder mixtures based on aluminate-rich, widely occurring pozzuolanas. According to the invention, the task is solved by the fact that the formation of calcium aluminate sulfate hydrates is not prevented as it is done in the known solutions, but is utilized for promoting the development of strength. This is done in the following way according to the invention: since, under the given conditions, not only the presence of lime is responsible for the formation of ettringite (tricalcium aluminate trisulfate hydrate), but its concentration

relationships too, the mixing ratio is adjusted so that the formation of ettringite is limited to the liquid phase. For this purpose, the property of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$) to bind a great deal of calcium during its formation is utilized. Under practical conditions, this is achieved by the choice of a corresponding binder composition, which permits the reduction of the calcium concentration during the solution phase by the absorption of calcium by the forming ettringite, to values below a limiting value which is to be determined later, so that destructive formation of ettringite cannot occur. Due to the decreasing availability of calcium, during the course of further hardening reactions - in contrast to the known solutions - low-calcium calcium aluminate and calcium silicate hydrates are formed. When exact predetermination of the quantitative relationships of the reactive substances cannot be done, then it is advisable to add a certain excess of the pozzuolanic component in order to exclude all risks relating to constant-volume hardening. Although, in this way, one cannot achieve the highest possible increase in strength, in comparison to the nonmodified gypsum products, there is still a considerable increase in strength. The following results, which were obtained on standard test specimens of a binder mixture of the invention according to Practical Example 1, illustrate this.

Development of the bending strength and compressive strength of standard prisms under comparable conditions with hindered drying:

storage and hardening time	bending strength (N/mm^2)		compressive strength (N/mm^2)	
	gypsum	gypsum-cement-pozzuolana	gypsum	gypsum-cement-pozzuolana
2 h	2.04	2.06	3.91	4.25
1 d	2.02	1.91	2.84	4.15
3 d	1.83	1.92	3.50	3.94
7 d	1.80	2.07	2.95	3.92
14 d	1.74	1.98	2.90	5.07
28 d	1.80	2.45	3.11	6.23

Thus, according to the invention, the conditions required for increasing the strength are created by the choice of a suitable ratio of the calcium-donating and calcium-binding

components, which, in the initial phase of hardening, ensure the high calcium concentration necessary for the formation of calcium aluminate sulfate hydrates, but, during the further progress of the hardening, decrease the calcium concentration to the extent that the formation of destructive calcium aluminate sulfate hydrates is avoided.

The task of the invention is to develop binder mixtures, the processing properties of which, especially the early strength, are determined predominantly by the sulfate component, through the formation of calcium sulfate dihydrate and calcium aluminate sulfate hydrate, the application properties of which, especially the final strength and the resistance to water, are significantly determined by the reaction products of the calcium-donating, hydraulic, and calcium-binding pozzuolanic components. With the aid of these binder mixtures, it is possible to produce structural parts which reach rapidly a strength where they can be handled and have improved final and wet strength in comparison to nonmodified gypsum products.

Predetermination of the suitable binder composition can be done by measurement of the change of the calcium concentration in the corresponding binder suspensions as a function of time or by measurement of the change of length on hardening mortar prisms. The measurement of the calcium concentration, which must not exceed in the binder suspension the maximum permissible calcium concentration values $K_1 > K_2$ at two suitable times $t_1 < t_2$, to be determined in more detail later, is somewhat more expensive, so that in most cases, measurement of the change of length proves to be more practical. Regarding the change of length under the conditions of hindered drying, a binder mixture according to the invention can be regarded as drying in a dimensionally stable manner when, after a hardening time of 7 days, the maximum permissible change in length does not exceed 0.5% and then a convergent length-time curve is observed.

The binder mixtures can be produced without additional energy or labor input by grinding the measured-out components together or by separately grinding them, followed by mixing.

According to the invention, this task was solved according to the characterizing part of Claim 1. Further advantageous embodiments of the invention are described in the Subclaims 2 to 8.

The hardening of such binder mixtures, when making up with water, proceeds in two different phases as a function of time. In the initial phase, it is based on the hydration of the calcium sulfate to calcium sulfate dihydrate and calcium aluminate trisulfate hydrate, and during the hydraulic post-hardening it is based on reactions between the calcium of the hydraulic component and the aluminates or silicates of the pozzuolanic component. Since the hydraulic post-hardening extends over a longer period of time, a part of the free water still present is bound as hydrate water, so that, in the case of water-binder ratios $w \leq 0.45$, for example, in a half-dry method using water depots (see DE-AS 29 19 311), technical drying of the end-product can be omitted. Preferably, natural pozzuolanas are used in the method according to the invention.

The progress of hardening during the first phase and the elasto-mechanical properties of the hardened products can be changed by adding suitable additives to the binder mixture.

The invention is explained below in more detail with the aid of 4 practical examples.

Example 1:

Binder, produced by grinding together and/or mixing, consisting of:
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Example 2:

Binder, consisting of:
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12 parts by weight of Portland cement or Portland clinker according to DIN 1164
18 parts by weight of trass meal according to DIN 51 043

Example 3:

Binder, consisting of:

60 parts by weight of hemihydrate gypsum plaster and/or gypsum plaster according to DIN 1168

13 parts by weight of Portland cement according to DIN 1164

27 parts by weight of trass meal according to DIN 51 043

Example 4:

Binder, consisting of:

60 parts by weight of hemihydrate gypsum plaster and/or gypsum plaster according to DIN 1168

25 parts by weight of trass cement according to DIN 1164

15 parts by weight of trass meal according to DIN 51 043

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Patent Claims:

1. Binder mixture of sulfate, calcium-donating and aluminosilicate-type pozzuolanic substances,
characterized by the fact
that it consists of 50 to 90 weight percent of calcium sulfate, 3 to 25 weight percent of calcium-donating substances and 5 to 35 weight percent of aluminosilicate-type pozzuolanic substances.

2. Binder mixture according to Claim 1,
characterized by the fact
that it contains hemihydrate gypsum plaster as sulfate component.

3. Binder mixture according to Claims 1 and 2,
characterized by the fact
that it contains Portland cement as hydraulic component.

4. Binder mixture according to Claims 1 to 3,
characterized by the fact
that it contains trass meal as pozzuolanic component.

5. Binder mixture according to Claims 1 to 4,
characterized by the fact
that the weight ratio of trass meal to Portland cement is within the limits of 1 to 2.

6. Binder mixture according to Claims 1 to 5,
characterized by the fact
that the processing and application properties are modified by additives.

7. Application of the binder mixture according to Claims 1 to 6,
characterized by the fact
that the first phase of the hardening, which proceeds in two phases in time, occurs with the application of pressure.

8. Application of the binder mixture according to Claims 1 to 7,
characterized by the fact
that a part of the still free water is bound chemically by the reaction products formed in the second hardening phase.

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